CONCENTRATIONS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN DETROIT RIVER SURFICIAL SEDIMENTS, 1991

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December 1994

FOREWORD

This report summarizes and provides a brief discussion of the polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) data for sediments collected from 26 stations during the 1991 Detroit River Sediment and Macrozoobenthic Community Assessment study by the (then) Ontario Ministry of the Environment (OMOE). The study was conducted as part of the Ministry's ongoing aquatic environmental assessment program, and in support of the Detroit River Remedial Action Plan (RAP).

Overall, the 1991 study was designed to evaluate the status of sediment quality and of benthic macroinvertebrate community health in the Detroit River, and by comparison with results from a similar study in 1980, to identify any trends in environmental quality.

A total of 77 stations distributed throughout the entire river were sampled during the 1991 study, and sediment samples were analyzed for metals, nutrients, solvent extractables, PCBs and organochlorine pesticides, chlorinated aliphatics and aromatics and polycyclic aromatic hydrocarbons. These sediment chemistry results, as well as the interpretation of the status of the benthic macroinvertebrate community relative to sediment quality, are contained in consultant's report released by the Ministry in 1993.

Based partly on results from the above chemical analyses, PCDD/F analysis was subsequently performed on duplicate, archived sediment samples from 12 of the original 77 stations. These analyses were completed in late 1993 and the results communicated by memorandum to the Detroit, St. Clair and St. Marys Rivers Team RAP office, to the Windsor District Office, and to the Sarnia District MISA Office. Samples from an additional 14 stations were analyzed for PCDD/F in 1994. In addition to the data on more routine trace contaminants, the overall selection of samples for PCDD/F analysis was based on the proximity of stations to major industrial or municipal dischargers and to the mouths of important tributaries, while also providing a broad geographic coverage of the river.

Detailed statistical analysis of the PCDD/F data in this report has not been performed. Nevertheless, the sediment data is being released to members of the Detroit River RAP and Stage 2 Task Teams in order to aid efforts to prioritize contaminated sediment areas and to identify sources and remediation measures for the river as part of the Stage 2 RAP process.

EXECUTIVE SUMMARY

This report presents information on sediment concentrations of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the Detroit River. The sediment samples were obtained during the 1991 Ministry of the Environment (OMOE) Detroit River Sediment and Macrozoobenthic Community Assessment Study. In all, 77 stations distributed throughout the entire river were sampled, and sediments were analyzed for metals, nutrients, solvent extractables, PCBs and organochlorine pesticides, chlorinated aliphatics and aromatics and polycyclic aromatic hydrocarbons. These sediment chemistry results and the interpretation of the status of the benthic macroinvertebrate community relative to sediment quality are included in a 1993 consultant's report released by the Ministry.

Based partly on results from the above chemical analyses, PCDD/F analyses were subsequently performed on duplicate, archived sediment samples from 13 Ontario and 13 Michigan stations. These stations were located near major industrial or municipal dischargers and near the mouths of important tributaries.

Elevated sediment concentrations of a variety of PCDD and PCDF congeners and isomers were found on both sides of the river. The two main locations along the Ontario shoreline were: upstream of the West Windsor Water Pollution Control Plant outfall and downstream of the General/Allied Chemicals discharges in Amherstburg. Expression of the 2,3,7,8-substituted isomer levels as their Toxicity Equivalent (TEQ) relative to 2,3,7,8-TetraCDD, showed that the Total 2,3,7,8-TetraCDD TEQ levels at four of the 13 Ontario stations were above the Ontario Recommended Maximum Total TEQ Guideline of 10 ppt for agricultural soils, with a range of 12 ppt to 29 ppt.

In general, higher concentrations of congeners and as well as toxic isomers were detected in Michigan nearshore sediments. For example, the Total 2,3,7,8-TetraCDD TEQs for 10 of the 13 Michigan stations were higher than the 10 ppt agricultural soil guideline, ranging from 18 ppt to 210 ppt. These stations included some from the Detroit area, and from downstream of the Rouge River and the Ecorse River discharges. The highest concentrations were, however, found downstream of the Great Lakes Steel plant in Ecorse, the Firestone Steel plant at Riverview in the Trenton Channel, and at the mouth of Monquagon Creek, which also discharges to the Trenton Channel. The Total TEQ concentrations for the stations downstream of Great Lakes Steel (100 ppt) and Monquagon Creek (210 ppt) were also at or above the Ontario Recommended Maximum Total TEQ Guideline of 100 ppt for sludge disposal.

The overall difference in concentrations of congeners, toxic isomers and Total 2,3,7,8-TetraCDD TEQs between the Ontario and Michigan stations was also evident in sediments at the mouth of the Detroit River, where the discharge enters Lake Erie. For example, the Total TEQ concentration downstream of the Trenton Channel was 39 ppt, about six times the level for the Ontario station located directly across the river.

ACKNOWLEDGEMENTS

The 1991 Detroit River study was a joint undertaking by the Great Lakes Section of the OMOE's Water Resources Branch (now the Surface Water Section of the OMOEE's Environmental Monitoring and Reporting Branch) and the Technical Assessment Unit of MOE's Southwestern Regional Office in London.

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1.0 INTRODUCTION

In 1991, the Ontario Ministry of the Environment (OMOE) conducted the Detroit River Sediment and Macrozoobenthic Community Assessment (Kauss and Thornley, 1991). This study was carried out in support of the Detroit River Remedial Action Plan. It was designed to evaluate the status of sediment quality and of macrozoobenthic (benthic macroinvertebrate) community health in the Detroit River, and by comparison with results from a similar study in 1980 (Thornley and Hamdy, 1984), to determine possible changes in environmental quality. A total of 77 stations distributed throughout the entire river were sampled, and sediments were analyzed for metals, nutrients, solvent extractables, PCBs and organochlorine pesticides, chlorinated aliphatics and aromatics and polycyclic aromatic hydrocarbons. These sediment chemistry results, as well as the interpretation of the status of the benthic invertebrate community relative to sediment quality, are contained in the Beak Consultants Limited report released by the Ministry in 1993 (Farara and Burt, 1993).

Based partly on results from the above chemical analyses, polychlorinated dibenz-p-dioxin and dibenzofuran (PCDD/F) analyses were subsequently performed on duplicate, archived sediment samples from 26 of the original 77 stations. The selection of stations was also based on their proximity to major industrial or municipal dischargers and important tributaries, while also providing broad geographic coverage of the river. This document summarizes and provides a brief discussion of the PCDD/F data from these stations. Although detailed statistical analysis of the PCDD/F data has not been performed, this information should be of use in the prioritization of contaminanted sediment areas and the identification of sources and appropriate remedial measures.

2.0 STUDY OBJECTIVES

Five overall project objectives were listed in the original project description (Kauss and Thornley, 1991). These were:

(i) What is (are) the present spatial pattern(s) of inorganic and organic contaminants in surficial sediments of the Detroit River, and to what degree does this correlate with the present benthic macroinvertebrate community?

(ii) Have there been any significant changes in sediment quality and benthos since 1980?

(iii) How toxic are contaminated sediments to indigenous sediment-dwelling biota and to laboratory test organisms, and what is the biological availability of sediment contaminants?

(iv) Is sediment quality still a limiting factor to improvement of the benthic community along the Ontario and Michigan shorelines of the Detroit River, or are current discharges still a problem?

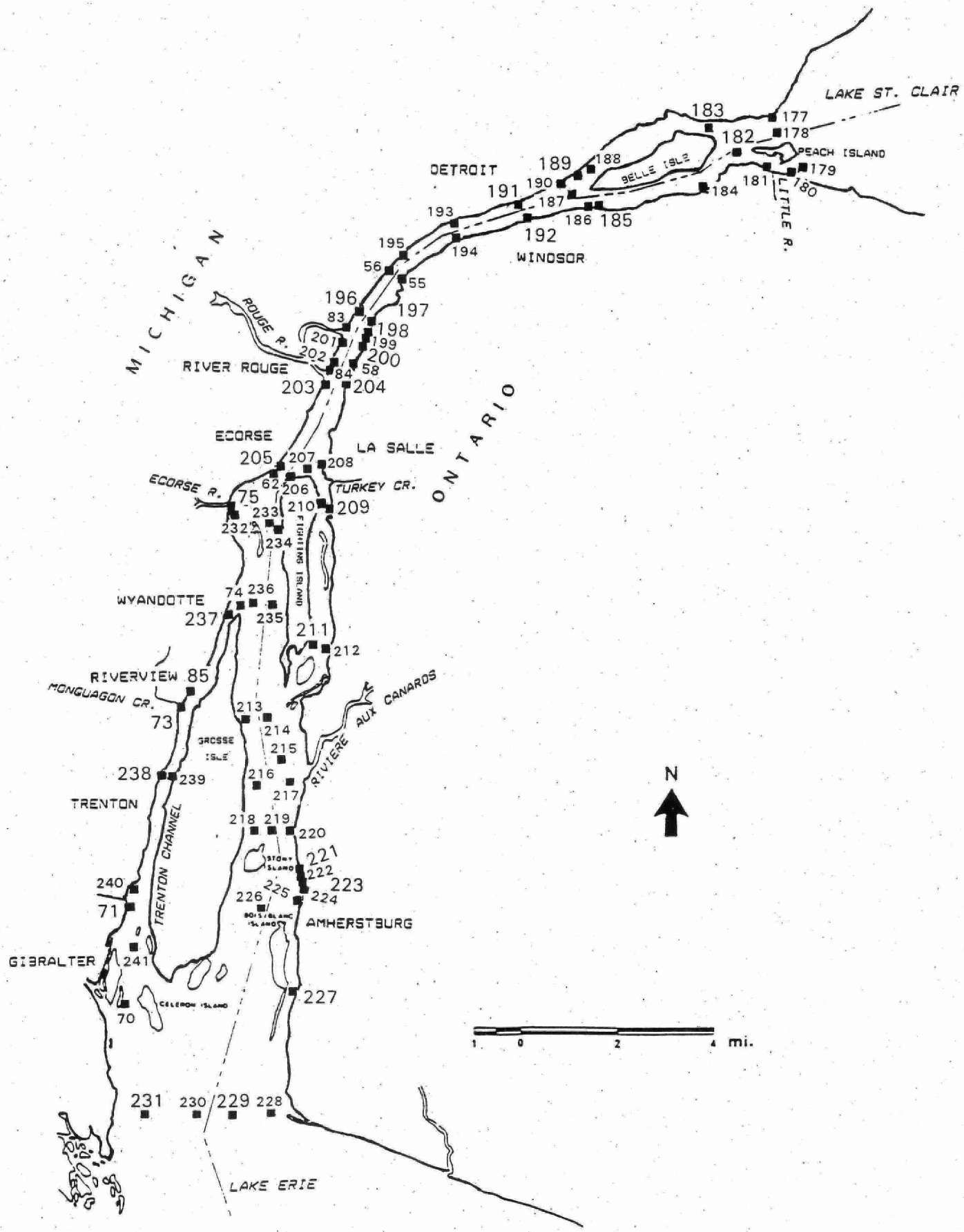

Figure 1. **1991 Detroit River Study Sediment Sampling Stations.** Station numbers in large type indicate that sediments were analyzed for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans.

Table 1. 1991 Detroit River Sampling Station Locations and Descriptions.

Station Number	Location / Description	Latitude (N)	Longitude (W)
182 (D)	600 m. west of Peche Island; 30 m. upstream of RGR"DPJ"IR buoy (ON)	42°20'45"	82°56'47"
183 (5)	60 m. downstream of Edison Yacht Club entrance and northwest of G"1A"FIG buoy; 400 m. downstream of Connors Creek; 30 m. off mainland (MI)	42°21'13"	82°57'32"
185 (8A)	40 m. upstream of Ford of Canada intake; 20 m. off mainland (ON)	42°19'39"	82°59'53"
189 (-)	west of pilings just downstream of U.S. Coast Guard slip, and upstream of sheet steel wall; 17 m. off mainland concrete wall (MI)	42°20'22"	83°00'30"
191 (F)	at Cobo Hall; opposite fourth support of overhead Detroit People Mover; 5 m. off mainland concrete wall (MI)	42°19'30"	83°02'53"
192 (12)	240 m. downstream of last Canadian National Railway ferry dock piling; 15 m. off mainland sheet steel wall (ON)	42°19'13"	83°02"31"
196 (17)	just upstream of Detroit Edison TGS, at TR3 Vertical Lights R2FR; under overhead cable; 8 m. off mainland concrete wall (MI)	42°17'36"	83°05'52"
197 (18)	upstream of Hearn Harbour Terminal, at TR3 Vertical Lights FR; under overhead cable; 12 m. off mainland (ON)	42°17'28"	83°05'28"
198 (-)	45 m. upstream of West Windsor WPCP outfall and downstream of Canadian Salt dock; 22 m. off mainland (ON)	42°17'13"	83°05'37"
200 (20)	200 m. downstream of West Windsor WPCP outfall, and opposite sand piles; 23 m. off mainland (ON)	42°17'06"	83°05'41"
203 (23)	at Detroit Edison TGS; 10 m. downstream of crib at Rouge River mouth; 15 m. off mainland (MI)	42°16'24"	83°06'36"
204 (24)	upstream of Morton Terminal; 22 m. off mainland (ON)	42°16'23"	83°06'00"
205 (26)	downstream of Great Lakes Steel plant , and just upstream of outfall; 45 m. off corner of concrete dock (MI)	42°14'48"	83°07'48"
209 (28)	downstream of Turkey Creek mouth; 224 m. south of Westport Marina; 25 m. off downstream corner of mainland sheet steel pier (ON)	42°14'16"	83°06'27"
211 (33)	20 m. off southeast end of Fighting Island; 1240 m. south-southwest of Grass Island (ON)	42°11'39"	83°06'43"
221 (-)	east of Amherstburg Channel; in embayment 20 m. upstream of General Chemical intake pumphouse; 27 m. off mainland (ON)	42°07'26"	83°06'52"
223 (-)	east of Amherstburg Channel; 200 m. downstream of General Chemical "chloride" outfall; 18 m. off mainland (ON)	42°07'14"	83°06'48"
227 (45)	east of Amherstburg Channel; 160 m. north of Bob-Lo Island dock; 125 m. off mainland, opposite motel (ON	42°05'15"	83°06'47"
229 (48)	west of Livingstone Channel; 1530 m. west of Bar Point, on DT 3.9 transect; 1470 m. south of Livingstone Channel west rock cut, and 220 m south of FIG"DL5 buoy (ON)	42°03'19"	83°08'08"
231 (50)	on DT 3.9 transect, 2030 m. south-southeast of Celeron Island; 1850 m. off mainland at Maple Beach (MI)	42°03'17"	83°09'49"
75 (-)	in Ecorse Channel, 5 m. downstream of Ecorse River mouth; 36 m. off mainland sheet steel wall (MI)	42°14'05"	83°08'52"
237 (36)	220 m. downstream of tip of cement wier at Wyandotte, west of Trenton Channel; 30 m. off mainland sheet steel wall (MI)	42°12'06	83°08'51"
85 (-)	80 m. downstream of tip of inlet south of Firestone Steel, just west of Trenton Channel; 215 m. upstream of north swing bridge; 22 m. off mainland (MI)	42°10'32"	83°09'47"
73 (-)	downstream of Monquagon Creek mouth, west of of Trenton Channel; 90 m. downstream of north swing bridge; 7 m. off mainland sheet steel wall (MI)	42°10'20"	83°09'55"
238 (O)	downstream of Edwin C. Levy, west of Trenton Channel; 355 m. upstream of G"13"FIG buoy; 20 m. off mainland (MI)	42°09'00"	83°10'21"
71 (-)	downstream of Chrysler Chemicals; 490 m. south-southwest of station 240, and 763 m. north-northeast of tip of Calf Island; 137 m. off mainland (MI)	42°06'42"	83°11'12"

NOTE: Station numbers in brackets represent corresponding OMOEE Southwestern Region numbers.
Geographic references, including buoy numbers, are as per NOAA chart 14853, March 9/85.
"ON" and "MI" indicate stations located in Ontario and Michigan waters, respectively.

(v) Are there still sufficient inputs of inorganic and organic contaminants to cause elevated levels in the tissues of introduced aquatic organisms?

The data in the present report mainly addresses objectives (i) and (iv).

3.0 METHODS

Sediment samples were obtained using a Shipek dredge. At each station, the top 3 cm. layers from each of three replicate grabs were composited in a stainless steel tray and thoroughly homogenized using a spatula. All sampling equipment was cleaned with solvent (hexane) and distilled water between stations. Subsamples of the homogenized sediment were placed in the stipulated sample jars (MOE, 1989) and shipped to the Ministry Laboratory Services Branch in Etobicoke for analysis. An extra subsample from each station was placed in an amber, solvent-rinsed jar and archived at -20°C until all regular analyses were completed. Archived samples from selected stations were subsequently submitted for PCDD/F analysis which was carried out according to documented procedures (OMOEE, 1993).

4.0 RESULTS AND DISCUSSION

When discharged to water, PCDDs and PCDFs tend to preferentially adsorb to solid organic carbon phases such as sediments. This tendency to partition onto fine particulate matter and/or organic matter increases with the degree of chlorination of the compound. In contrast, volatility and water solubility decrease as chlorination increases (Mackay *et al.*, 1992).

4.1 Congener Group Concentrations:

The percentages of silt and clay (<62 μm diameter particles) in the Detroit River sediment samples ranged from 2.4% to 94% and from 0.8% to 7.3% total organic carbon (TOC). Total PCDD/F congener group concentrations (as indicated by "Total PCDDs + PCDFs" in Figure 2) were most strongly correlated with the percentage of fine particles in sediments (Figure 2A). The similar slopes of the regression lines for the Michigan and Ontario stations indicate that, on average and at a given silt and clay percentage, the concentration of Total PCDDs + PCDFs was nearly 900 ppt higher along the Michigan shoreline. The relationship of PCDD/F concentrations with organic carbon was not as significant as with silt and clay, particularly for the Ontario stations, which did not have as great a range in TOC concentrations as the Michigan stations (Figure 2B).

Total PCDD + PCDF congener group concentrations were lowest at: station 192 (210 ppt), located below the Canadian National Railway ferry dock; at the upstream control station 183 (252 ppt) located just downstream of Connors Creek in Michigan; at station 211 (299 ppt), at the southern end of Fighting Island in Ontario; and at station

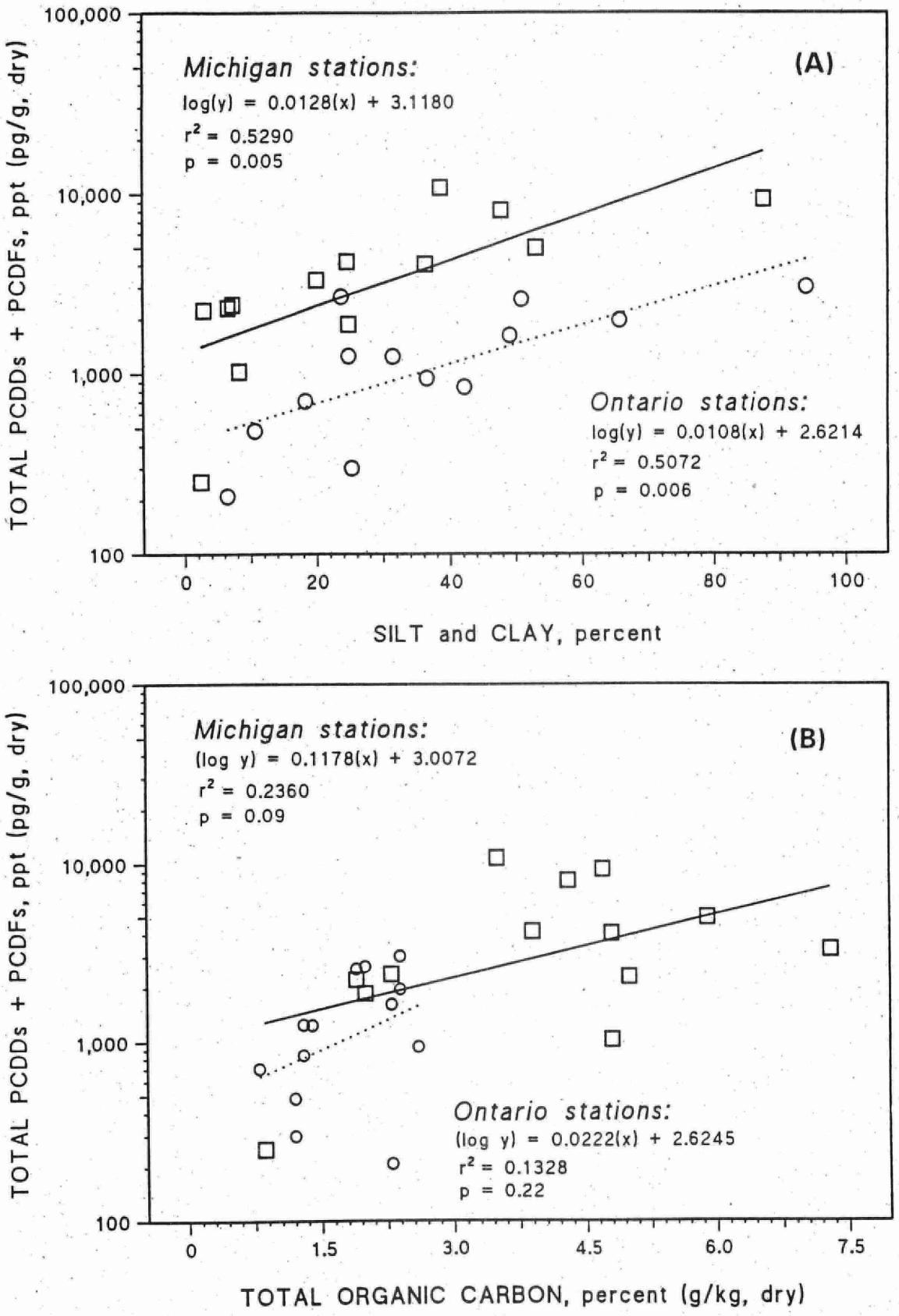

Figure 2. **Relationship between Concentration of Total PCDD + PCDF Congeners and: (A) Silt and Clay, and (B) Total Organic Carbon in 1991 Detroit River Surficial Sediment Samples.** Included are lines of best fit for the Michigan (solid line, squares) and Ontario stations (dotted line, circles).

221 (483 ppt), just upstream of the General/Allied Chemicals water intake in Amhestburg.

The highest Total PCDDs + PCDFs concentrations along the Ontario nearshore were found at: station 198 (3,033 ppt), just upstream of the West Windsor Water Pollution Control Plant (WPCP) discharge; and at stations 223 and 227, downstream of the General/Allied Chemicals discharges near Amherstburg. Levels in Michigan nearshore sediments were somewhat higher than in Ontario. For example, at stations 189, 191, 196 and 203 along the Detroit shoreline, the total concentration of the 10 congener groups ranged from 2,241 ppt to 4,168 ppt. The highest and third-highest Total PCDDs + PCDFs concentrations of the study were found at stations 205 (10,800 ppt) and 85 (8,070 ppt) located downstream of the Great Lakes Steel and Firestone Steel plants in Ecorse and Riverview, respectively. The second-highest concentration was detected in sediment from station 73 (9,302 ppt), immediately downstream of the Monquagon Creek discharge, also in Riverview.

The difference in the Total PCDDs + PCDFs concentrations between Ontario and Michigan stations was also evident in the concentration gradient at the outlet of the river near Lake Erie: the concentration of all 10 congener groups at station 229 west of the Livingstone Shipping Channel (706 ppt) was less than half that at station 231 (1,867 ppt) south of the Trenton Channel.

The environmental persistance of PCDDs and PCDFs increases with increasing chlorination (Mackay *et al.*, 1992) whereas the more toxic, less chlorinated componds appear to be less stable (Czucwa and Hites, 1986). In the Detroit River, the octachloro (8 chlorine)-substituted PCDD congener (and 2,3,7,8-substituted isomer) was usually the most abundant in sediments, followed by 7 chlorine-, 6-chlorine, and then, if present, by either 5- or 4 chlorine-substituted congeners. In the case of PCDF congeners, concentrations of the 7 chlorine-substituted congeners were usually the highest, followed by 6-, 5- and 4 chlorine-substituted congeners. Exceptions to this trend were, however found at stations 182, 197, 85, 73 and 71, where concentrations of 8 chlorine-substituted PCDD and PCDF congeners were the highest Tables 2 and 3).

4.2 Toxic (2,3,7,8-Substituted) Isomer Concentrations:

Sixteen of the seventeen possible toxic (i.e., 2,3,7,8-substituted) isomers were detected in sediment samples from one or more of the 26 Detroit River stations. Sediment from station 205 downstream of Great Lakes Steel contained the highest levels of 2,3,7,8-substituted dioxin isomers and the second-highest concentrations of 2,3,7,8-substituted furan isomers; the reverse was the case for station 73 immediately downstream of Monquagon Creek (Table 3). The most toxic isomer, 2,3,7,8-TetraCDD, was only detected in sediments from Michigan stations 205 and 73 at 22 ppt and 18 ppt, respectively. The isomer 1,2,3,7,8-PentaCDD, with half the toxicity of 2,3,7,8-TetraCDD, was also restricted to these two stations, at concentrations of 29 ppt and 13 ppt, respectively.

Table 2. **Surficial Sediment Concentrations of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans at Ontario Stations in the Detroit River, 1991.**
Concentrations are in ppt = pg/g (10^{-12} g/g) dry sediment.

Parameter	I-TEF	Station 182 (D)	185 (8A)	192 (12)	197 (18)	198 (--)	200 (20)	204 (24)	209 (28)	211 (33)	221 (--)	223 (--)	227 (45)	229 (48)
		Congener Groups												
TetraCDD	--	nd(1)	1.6^{1}	nd(1)	3.6^{2}	nd(3)	nd(2)	nd(1)	nd(1)	nd(1)	nd(1)	19^{6}	9.0^{4}	5.3^{3}
PentaCDD	--	nd(3)	6.4^{4}	nd(2)	6.0^{3}	11^{3}	nd(4)	3.3^{1}	5.0^{3}	nd(1)	nd(1)	nd(4)	7.3^{4}	6.9^{4}
HexaCDD	--	22^{3}	52^{6}	17^{3}	29^{4}	64^{6}	38^{3}	150^{6}	47^{5}	5.0^{2}	9.0^{2}	40^{5}	52^{6}	48^{5}
HeptaCDD	--	82^{2}	120^{2}	34^{2}	130^{2}	230^{2}	140^{2}	450^{2}	120^{2}	25^{2}	34^{2}	190^{2}	180^{2}	89^{2}
OctaCDD *	--	680	810	130	1300	2500	1400	500	670	260	440	920	2000	330
TetraCDF	--	nd(3)	37^{7}	nd(2)	22^{7}	43^{8}	100^{12}	6.6^{3}	23^{8}	nd(2)	nd(1)	1000^{19}	160^{15}	60^{11}
PentaCDF	--	6.6^{1}	96^{7}	7.0^{2}	18^{5}	35^{6}	84^{8}	17^{3}	18^{5}	2.1^{1}	nd(3)	320^{14}	75^{12}	43^{8}
HexaCDF	--	7.3^{1}	58^{7}	12^{2}	20^{6}	50^{6}	97^{7}	36^{4}	20^{5}	1.6^{1}	nd(3)	99^{9}	34^{6}	43^{6}
HeptaCDF	--	22^{2}	38^{2}	10^{2}	30^{4}	53^{4}	64^{4}	56^{2}	24^{2}	5.6^{2}	nd(4)	39^{4}	33^{4}	54^{3}
OctaCDF *	--	24	22	nd(5)	63	47	52	30	18	nd(6)	nd(4)	24	23	27
Total PCDDs + PCDFs:		**843.9**	**1241**	**210.0**	**1622**	**3033**	**1975**	**1249**	**945.0**	**299.3**	**483.0**	**2651**	**2573**	**706.2**
		2,3,7,8- Substituted Isomers												
2,3,7,8-TetraCDD	1.0	nd(1)	ND(1)	nd(1)	nd(1)	nd(2)	nd(1)	nd(1)	nd(1)	nd(1)	nd(1)	nd(2)	1.5	nd(1)
1,2,3,7,8-PentaCDD	0.5	nd(1)	1.2	nd(1)	nd(1)	nd(2)	nd(2)	nd(1)	nd(1)	nd(1)	nd(1)	nd(2)	1.7	1.4
1,2,3,4,7,8-HexaCDD	0.1	nd(1)	1.2	nd(1)	nd(1)	3.3	nd(1)	nd(1)	nd(1)	nd(1)	nd(1)	nd(1)	1.6	nd(1)
1,2,3,6,7,8-HexaCDD	0.1	nd(2)	5.1	nd(2)	3.0	4.5	nd(4)	16	4.8	nd(1)	nd(1)	3.7	4.5	5.3
1,2,3,7,8,9-HexaCDD	0.1	nd(3)	4.0	nd(1)	nd(4)	6.9	nd(4)	6.8	3.6	nd(1)	nd(1)	3.1	4.9	2.8
1,2,3,4,6,7,8-HeptaCDD	0.01	35	55	14	57	97	64	130	52	11	14	71	75	41
1,2,3,4,6,7,8,9-OctaCDD	0.001	680	810	130	1300	2500	1400	500	670	260	440	920	2000	330
2,3,7,8-TetraCDF **	0.1	nd(3)	5.4	nd(1)	6.0	11	38	3.2	6.3	nd(2)	nd(1)	67	28	9.6
1,2,3,7,8-PentaCDF	0.05	nd(2)	1.6	nd(1)	1.9	6.8	24	nd(1)	2.1	nd(1)	nd(1)	22	6.1	2.3
2,3,4,7,8-PentaCDF	0.5	nd(1)	2.3	nd(1)	2.1	4.9	13	nd(1)	1.9	nd(1)	nd(1)	27	5.9	3.5
1,2,3,4,7,8-HexaCDF **	0.1	nd(4)	4.1	nd(1)	4.4	15	43	3.7	4.7	nd(2)	nd(2)	24	9.3	6.1
1,2,3,6,7,8-HexaCDF	0.1	nd(2)	2.4	nd(1)	1.8	5.5	13	nd(1)	1.6	nd(1)	nd(1)	12	3.5	2.3
2,3,4,6,7,8-HexaCDF	0.1	nd(2)	2.7	nd(2)	1.9	4.8	6.9	nd(1)	nd(1)	nd(1)	nd(1)	11	2.4	2.1
1,2,3,7,8,9-HexaCDF	0.1	nd(1)	nd(1)	nd(1)	nd(1)	nd(1)	nd(1)	nd(1)	nd(1)	nd(1)	nd(1)	nd(2)	nd(1)	nd(1)
1,2,3,4,6,7,8-HeptaCDF	0.01	14	17	3.7	15	27	34	24	12	3.2	nd(4)	19	16	25
1,2,3,4,7,8,9-HeptaCDF	0.01	nd(1)	nd(2)	nd(1)	2.0	3.2	6.8	nd(2)	nd(1)	nd(1)	nd(1)	2.5	2.1	1.9
1,2,3,4,6,7,8,9-OctaCDF	0.001	24	22	nd(5)	63	47	52	30	18	nd(6)	nd(4)	24	23	27
Total 2,3,7,8-TetraCDD TEQ:		**1.2**	**5.9**	**0.3**	**5.0**	**12**	**20**	**5.0**	**4.5**	**0.4**	**0.6**	**29**	**14**	**6.4**

NOTES: Concentrations are corrected for recovery of isotopically-labelled standards.
nd = not detected; detection limit in ppt given in brackets ( ).
Superscripts indicate the number of isomers detected.
* = comprised of only one isomer (1,2,3,4,6,7,8,9-).
** = maximum possible concentration due to potential chromatographic overlap.
I-TEF = International Toxic Equivalence Factor; TEQs calculated assuming that "nd" = zero.
Station numbers in brackets ( ) are the corresponding Southwestern Region designations.

Table 3. **Surficial Sediment Concentrations of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans at Michigan Stations in the Detroit River, 1991.** Concentrations are in ppt = pg/g (10^{-12} g/g) dry sediment.

Parameter	I-TEF	Station 183 (5)	189 (--)	191 (F)	196 (17)	203 (23)	205 (26)	237 (36)	75 (--)	85 (--)	73 (--)	238 (O)	71 (--)	231 (50)
		Congener Groups												
TetraCDD	--	nd(1)	nd(6)	24^{5}	nd(4)	nd(10)	150^{6}	1.7^{1}	23^{7}	130^{3}	62^{5}	30^{3}	23^{6}	24^{5}
PentaCDD	--	nd(1)	20^{2}	45^{6}	6.5^{1}	34^{2}	240^{6}	5.0^{3}	29^{7}	110^{11}	110^{7}	37^{2}	27^{4}	23^{5}
HexaCDD	--	14^{3}	130^{4}	290^{6}	6.5^{1}	120^{3}	1400^{4}	48^{5}	220^{7}	490^{6}	810^{4}	300^{4}	190^{5}	180^{6}
HeptaCDD	--	41	360^{2}	350^{2}	470^{2}	290^{2}	1900^{2}	120^{2}	360^{2}	650^{2}	1100^{2}	500^{2}	260^{2}	170^{4}
OctaCDD *	--	140	1300	860	3400	1800	4900	730	1100	1800	2500	1800	820	650
TetraCDF	--	3.0^{1}	140^{7}	89^{14}	33^{3}	270^{13}	520^{12}	28^{8}	130^{15}	290^{15}	1400^{14}	360^{10}	180^{15}	190^{16}
PentaCDF	--	10^{2}	110^{5}	140^{10}	48^{4}	250^{7}	320^{8}	22^{5}	140^{10}	380^{16}	960^{10}	260^{7}	140^{11}	150^{9}
HexaCDF	--	14^{3}	280^{6}	180^{9}	84^{2}	480^{5}	490^{6}	23^{6}	100^{7}	480^{9}	720^{7}	500^{7}	190^{10}	180^{6}
HeptaCDF	--	19^{2}	660^{2}	180^{3}	120^{2}	640^{2}	560^{2}	28^{2}	130^{4}	740^{4}	640^{4}	630^{3}	190^{4}	170^{2}
OctaCDF *	--	11	290	83	nd(100)	170	320	21	80	3000	1000	560	390	130
Total PCDDs + PCDFs:		**252.0**	**3290**	**2241**	**4168**	**4054**	**10800**	**1027**	**2312**	**8070**	**9302**	**4977**	**2410**	**1867**
		2,3,7,8- Substituted Isomers												
2,3,7,8-TetraCDD	1.0	nd(1)	nd(3)	3.2	nd(4)	nd(2)	22	nd(1)	3.3	nd(4)	18	nd(3)	4.0	6.0
1,2,3,7,8-PentaCDD	0.5	nd(1)	nd(2)	5.2	nd(2)	nd(2)	29	nd(1)	5.0	9.8	13	nd(6)	4.7	4.9
1,2,3,4,7,8-HexaCDD	0.1	nd(1)	nd(6)	2.3	nd(4)	nd(4)	nd(4)	nd(1)	2.9	5.5	nd(6)	nd(5)	nd(2)	1.9
1,2,3,6,7,8-HexaCDD	0.1	1.9	12	26	6.5	14	130	4.8	26	56	73	130	20	20
1,2,3,7,8,9-HexaCDD	0.1	nd(1)	8.2	16	nd(4)	nd(8)	57	4.0	15	29	nd(40)	nd(10)	11	11
1,2,3,4,6,7,8-HeptaCDD	0.01	21	190	160	210	130	880	55	180	310	500	230	130	110
1,2,3,4,6,7,8,9-OctaCDD	0.001	140	1300	860	3400	1800	4900	730	1100	1800	2500	1800	820	650
2,3,7,8-TetraCDF **	0.1	3.0	nd(5)	14	8.5	12	46	6.9	25	72	320	73	47	56
1,2,3,7,8-PentaCDF	0.05	nd(1)	4.4	3.2	nd(2)	9.5	16	1.9	3.8	43	250	73	30	19
2,3,4,7,8-PentaCDF	0.5	nd(1)	6.0	6.6	nd(3)	12	24	2.3	9.5	28	170	34	18	19
1,2,3,4,7,8-HexaCDF **	0.1	nd(2)	39	14	nd(10)	45	67	4.1	11	110	310	130	71	66
1,2,3,6,7,8-HexaCDF	0.1	nd(1)	7.2	6.2	nd(7)	nd(10)	20	1.6	4.8	28	65	43	16	15
2,3,4,6,7,8-HexaCDF	0.1	nd(1)	16	5.5	nd(6)	30	33	1.8	5.3	nd(10)	39	22	5.4	5.4
1,2,3,7,8,9-HexaCDF	0.1	nd(1)	nd(4)	ND(1)	nd(6)	nd(2)	nd(5)	nd(1)	nd(1)	2.7	nd(4)	nd(6)	2.2	nd(1)
1,2,3,4,6,7,8-HeptaCDF	0.01	8.1	340	68	44	350	200	13	53	280	270	220	74	74
1,2,3,4,7,8,9-HeptaCDF	0.01	nd(1)	nd(10)	5.9	nd(4)	nd(5)	nd(20)	nd(1)	3.7	32	56	34	20	13
1,2,3,4,6,7,8,9-OctaCDF	0.001	11	290	83	nd(100)	170	320	21	80	3000	1000	560	390	130
Total 2,3,7,8-TetraCDD TEQ:		**0.9**	**18**	**21**	**7.4**	**23**	**100**	**5.0**	**23**	**62**	**210**	**68**	**38**	**39**

NOTES: Concentrations are corrected for recovery of isotopically-labelled standards.
nd = not detected; detection limit in ppt given in brackets ( ).
Superscripts indicate the number of isomers detected.
* = comprised of only one isomer (1,2,3,4,6,7,8,9-).
** = maximum possible concentration due to potential chromatographic overlap.
I-TEF = International Toxic Equivalence Factor; TEQs calculated assuming that "nd" = zero.
Station numbers in brackets ( ) are the corresponding Southwestern Region designations.

4.3 Potential Sediment Toxicity:

The widely-differing toxicities of the various 2,3,7,8-substituted PCDD and PCDF isomers makes comparison of the different stations on the basis of their toxicological significance, or potential toxicity, difficult. Therefore, Toxicity Equivalent (TEQ) concentrations were determined for each isomer using the International Toxicity Equivalency Factors listed in Tables 2 and 3 to convert to the equivalent concentration of 2,3,7,8-TetraCDD. In these calculations, a value of "zero" was substituted for "nd", which may have resulted in some underestimates of the actual TEQs (e.g., for stations 196, 73 and 238). Although direct comparison of these calculated aquatic sediment TEQs to terrestrial soil guidelines is perhaps not recommended, it does provide some measure of the relative impairment of sediments. The resultant spatial distribution of TEQs along the Ontario and Michigan shorelines (Figure 3B) is somewhat similar to that observed for Total PCDDs + PCDFS (Figure 3A), although the former provides a much better picture of the potential toxicity of the sediments. Sediments at four of the 13 Ontario stations contained Total 2,3,7,8-TetraCDD TEQs above the Ontario Recommended Maximum Total TEQ Guideline of 10 ppt for agricultural soils. These were stations 198, 200, 223 and 227, with Total TEQs ranging from 12 ppt to 29 ppt. Maxima of 20 ppt and 29 ppt were found at stations 200 and 223, located downstream of the West Windsor WPCP and the General Chemicals chloride sewer, respectively (see Tables 2 and 3, and Figure 3B).

Sediments at 10 of the 13 Michigan stations had Total 2,3,7,8-TetraCDD TEQ concentrations that exceeded the 10 ppt Guideline for agricultural soils. Levels at stations 189, 191, 203 and 75, located downstream of the U.S. Coast Guard slip, at Cobo Hall, downstream of the Rouge River at Detroit Edison, and downstream of the Ecorse River, respectively, ranged between 18 ppt and 23 ppt. The second- and fourth-highest Total TEQ concentrations were detected at stations 205 and 85, downstream of Great Lakes Steel (100 ppt) and Firestone Steel (62 ppt) discharges, respectively. The study maximum of 210 ppt was found at station 73, just downstream of Monquagon Creek. It should be noted that the Total 2,3,7,8-TetraCDD TEQs at stations 205 and 73 were also at or higher than the Recommended Maximum Guideline of 100 ppt for sludge disposal. They were, however, below the Recommended Maximum Total TEQ Guideline of 1,000 ppt for urban/industrial soils. Total TEQ levels at stations 238, 71 and 231, located further downstream in the Trenton Channel and near Lake Erie, decreased from 68 ppt to 39 ppt; however, the latter was about six times higher than at the Ontario station (6.4 ppt) located directly across the river.

Provincial Aquatic Sediment Quality Guidelines for individual 2,3,7,8-substituted isomers or for total 2,3,7,8-TetraCDD TEQ are not yet available; however, Tentative Guidelines have been derived for many of the isomers. Comparison with these shows that concentrations of 2,3,7,8-TetraCDD at stations 205 (22 ppt) and 73 (18 ppt), and of 2,3,7,8-TetraCDF (320 ppt) and 2,3,4,7,8-PentaCDF (170 ppt) at station 73, are slightly above the Tentative Aquatic Sediment Quality 'No Effect Level' Guidelines for these three isomers (R. Jaagumagi, Standards Development Branch, pers. comm.).

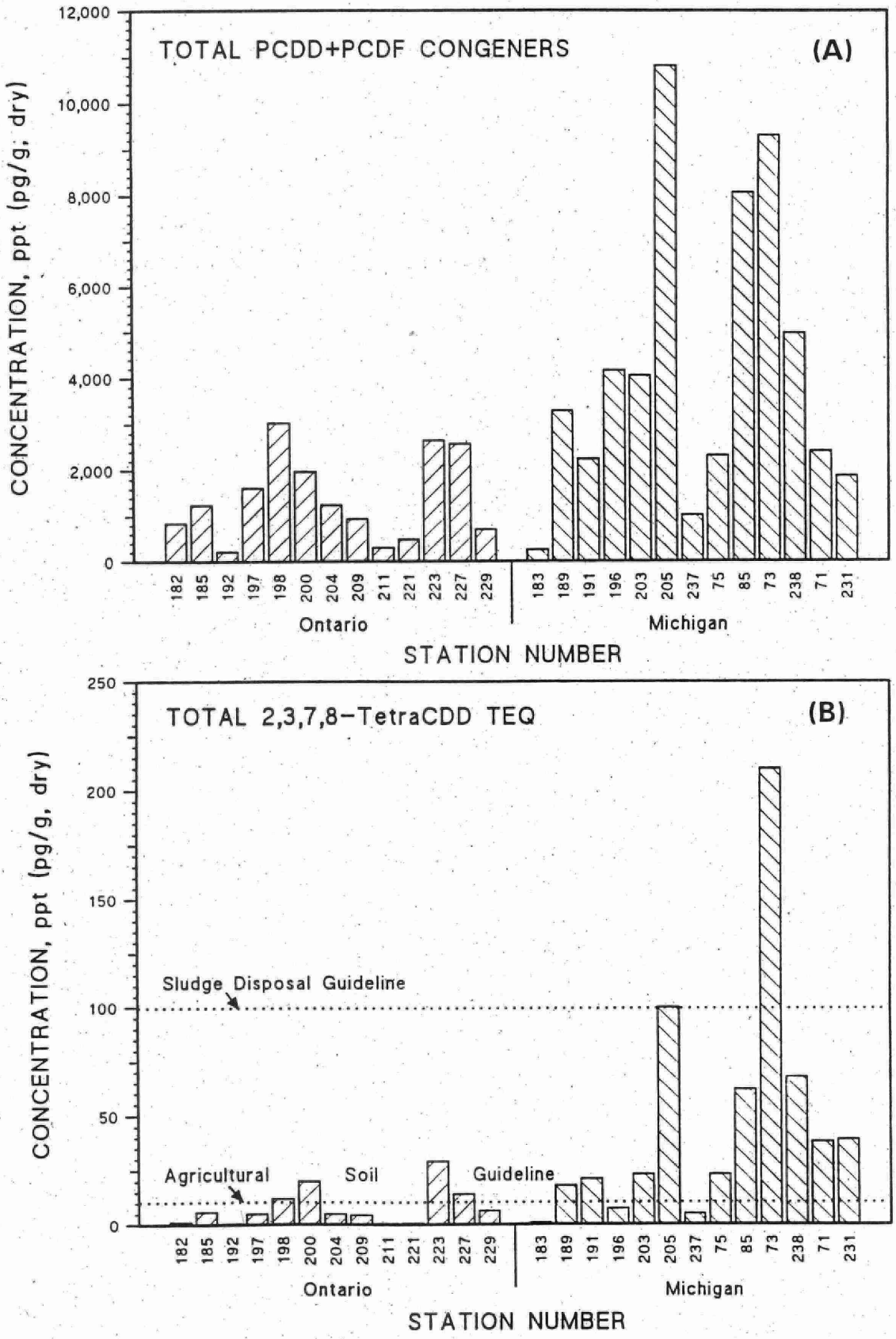

Figure 3. **Distribution of Concentrations of: (A) Total PCDD + PCDF Congeners, and (B) Total 2,3,7,8-TetraCDD TEQs in 1991 Detroit River Surficial Sediment Samples.** Ontario and Michigan stations are in separate groups; within each group, station sequence is from upstream (left) to downstream (right).

4.4 Comparison with other Areas of Concern:

The relative magnitude, and importance, of these Detroit River sediment data can be put into perspective by comparison with concentrations in sediments of two other Great Lakes Areas of Concern that have similar industrial development. These are the St. Clair River, which is upstream of the Detroit River and connects Lake Huron with Lake St. Clair, and the Niagara River, which connects Lakes Erie and Ontario.

The range of the congener group and 2,3,7,8-substituted isomer concentrations in the 1991 Detroit River sediment samples were similar to the corresponding values detected in 1991 St. Clair River samples (see Table 4). However, the St. Clair River

Table 4. Comparison of PCDD/F Congener Group, 2,3,7,8-Substituted Isomer and Total 2,3,7,8-TetraCDD TEQ Concentrations in Detroit River Sediments with Values in the St. Clair and Niagara Rivers.
Concentrations are in ppt = pg/g (10^{-12} g/g) dry sediment.

Parameter	**Detroit River**, 1991 (this study)	**St. Clair River**, 1990 (RAP Stage 1 update)	**Niagara River**, 1993 (Richman, 1994)
TetraCDD	nd(1) - 150	nd(1) - 420	nd(4) - 110,000
PentaCDD	nd(1) - 240	nd(1) - 170	nd(7) - 77,000
HexaCDD	9.0 - 1,400	nd(3) - 320	110 - 420,000
HeptaCDD	34 - 1,900	8.2 - 420	810 - 560,000
OctaCDD *	130 - 4,900	36 - 1,200	8,200 - 320,000
TetraCDF	nd(1) - 1,400	1.6 - 1,900	22 - 110,000
PentaCDF	nd(3) - 960	nd(1) - 300	28 - 180,000
HexaCDF	nd(3) - 720	nd(2) - 1,200	47 - 450,000
HeptaCDF	nd(4) - 660	4.4 - 1,600	230 - 800,000
OctaCDF *	nd(4) - 3,000	nd(12) - 7,100	200 - 1,100,000
Total PCDDs + PCDFs	252 - 10,800	81.7 - 14,630	873.7 - 2,825,000
2,3,7,8-TetraCDD	nd(1) - 22	nd(1 - 17)	nd(4) - 100,000
1,2,3,7,8-PentaCDD	nd(1) - 29	nd(1) - 2.3	nd(1) - 3,400
1,2,3,4,7,8-HexaCDD	nd(1) - 5.5	nd(1 - 23)	nd(1) - 10,000
1,2,3,6,7,8-HexaCDD	nd(1) - 130	nd(1) - 5.1	11 - 90,000
1,2,3,7,8,9-HexaCDD	nd(1) - 57	nd(1) - 2.0	4.0 - 57,000
1,2,3,4,6,7,8-HeptaCDD	11 - 880	4.2 - 220	55 - 390,000
1,2,3,4,6,7,8,9-OctaCDD	130 - 4,900	36 - 1,200	240 - 320,000
2,3,7,8-TetraCDF **	nd (1) - 320	nd(3) - 110	nd(1) - 20,000
1,2,3,7,8-PentaCDF	nd(1) - 250	nd(1) - 11	nd(1) - 9,400
2,3,4,7,8-PentaCDF	nd(1) - 170	nd(1) - 7.3	3.1 - 15,000
1,2,3,4,7,8-HexaCDF	nd(1) - 310	nd(1) - 310	nd(10) - 230,000
1,2,3,6,7,8-HexaCDF	nd(1) - 65	nd(1) - 69	nd(4) - 48,000
2,3,4,6,7,8-HexaCDF	nd(1) - 39	nd(1) - 82	nd(2) - 5,000
1,2,3,7,8,9-HexaCDF	nd(1) - 2.7	nd(1) - 8.6	nd(1) - 1,600
1,2,3,4,6,7,8-HeptaCDF	nd(4) - 350	3.8 - 820	56 - 700,000
1,2,3,4,7,8,9-HeptaCDF	nd(1) - 56	nd(1) - 160	nd(9) - 26,000
1,2,3,4,6,7,8,9-OctaCDDF	nd(4) - 3,000	6.0 - 7,100	120 - 1,100,000
Total 2,3,7,8-TetraCDD TEQ:	0.3 - 210	0.2 - 77	17 - 140,000

NOTES: Concentrations are corrected for recovery of isotopically-labelled standards.
nd = not detected; detection limit in ppt given in brackets ( ).
* = comprised of only a single isomer (1,2,3,4,6,7,8,9-).
** = maximum possible concentration due to potential chromatographic overlap.
Total 2,3,7,8-TetraCDD TEQ calculated using I-TEFs, assuming that "nd" = zero; see Tables 2 and 3.

maxima for Penta-, Hexa-, Hepta- and OctaCDD, and Penta CDF congeners and isomers were usually lower than the corresponding maxima in the Detroit River. In contrast, the maximum TetraCDD and Hexa-, Hepta- and OctaCDF congener and isomer concentrations in the St. Clair River were usually higher than in the Detroit River. It is noteworthy, however, that the Detroit River (and the St. Clair River) maxima for congeners as well as 2,3,7,8-substituted isomers were well below the highest concentrations found in Niagara River sediments, near some hazardous waste sites. The maximum Total 2,3,7,8-TetraCDD TEQ for the Detroit River (210 ppt) was, however, about three times higher than the corresponding value for the St. Clair River (77 ppt).

5.0 CONCLUSIONS AND RECOMMENDATIONS

Elevated surficial sediment concentrations of a variety of PCDD and PCDF congeners and toxic isomers were found on both sides of the Detroit River, indicating the presence of relatively recent inputs of these contaminants. The two main locations along the Ontario shoreline were: upstream of the West Windsor Water Pollution Control Plant outfall and downstream of the General/Allied Chemicals discharges in Amherstburg. In general, higher concentrations of congeners as well as toxic isomers were detected in Michigan nearshore sediments. These included stations from the Detroit waterfront area, downstream of the Rouge River, downstream of the Great Lakes Steel plant in Ecorse, the Ecorse River, the Firestone Steel plant at Riverview in the Trenton Channel, and at the mouth of Monquagon Creek, which also discharges to the Trenton Channel. The PCDD/F contamination of Detroit River sediments, and the overall higher concentrations at Michigan stations was also evident in sediments collected at the mouth of the Detroit River, where the discharge enters Lake Erie. *The sources of PCDDs and PCDFs to the above-noted areas of the Detroit River, and ultimately to Lake Erie, should be identified and appropriate remediation efforts initiated as soon as possible.*

Although provincial sediment quality guidelines are not yet available for these compounds, the calculated Total 2,3,7,8-TetraCDD TEQ concentrations at four of the 13 Ontario stations were above the Ontario Recommended Maximum Total TEQ Guideline of 10 ppt for agricultural soils. In contrast, the Total 2,3,7,8-TetraCDD TEQ in sediments from 10 of the 13 Michigan stations was above the 10 ppt agricultural soil guideline; levels at two of the 13 stations were also at or above the Ontario Recommended Maximum Total TEQ Guideline of 100 ppt for sludge disposal. In addition, concentrations of three toxic isomers were slightly above Tentative provincial Sediment Quality Guidelines at the two Michigan stations with the highest concentrations of PCDDs and PCDFs. *The availability of published, biologically-based Sediment Quality Guidelines would greatly assist in the interpretation of these sediment data. Also, information on PCDD and PCDF (congener and toxic isomer) concentrations in resident forage and sport fish species should be obtained to determine if this resource is being impacted by the presence of these contaminants in the river system.*

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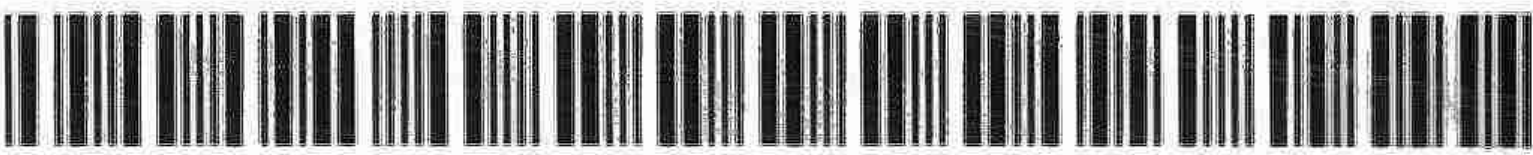
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